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HPC Paper

(Statement A)

NEW MATERIALS DESIGN

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Abstract

Progress has been made on several projects under the Challenge Project award. In the area of high energy density materials, calculations are under way on Al atoms embedded in clusters of H₂ molecule. These calculations are very demanding, since very large basis sets and high levels of theory are required to obtain sufficient accuracy for these weakly bound species. Potential energy surfaces are being determined to assess the mobility of an Al atom in H₂ matrices. Similar analyses are underway for B, Be, and Mg atoms. In another HEDM project, a series of large, nitrogen-containing rings, suggested as HEDM targets by Dr. Rob Schmitt at SRI, are being studied. The first of these has been shown to have a very large heat of formation and specific impulse, so it is a very promising species. Calculations on the second compound are in progress. Subsequent calculations will analyze the sensitivity of these compounds to environmental interactions (e.g., hydrolysis, acid/base attack, oxygen). Calculations of the structures and hydrogen bonding interactions present in 1,1-diamino-2,2-dinitroethene, a new energetic material with low friction sensitivity, are also underway.

Since solid hydrogen doped with energetic impurities may form the basis for an additional class of HEDM to be used in rocket propulsion applications, a key research priority is therefore the largescale computer simulation of impurity diffusion and recombination in HEDM in order to better understand the reasons for its stability, or instability, as the case may be. The recombination of atomic impurities is an extremely exothermic reaction, and therefore thermodynamically favored. Theoretical developments within the Voth research group allow the (otherwise impossible) quantum dynamical simulation of these systems which is necessary to properly treat the problem. These methods have been implemented in a highly scalable algorithm for execution on the various DoD HPC platforms. The results of quantum computer simulations will be reported which probe for the first time the stability and dynamics of solid hydrogen systems containing multiple atomic lithium and boron impurities. The instability point for the case of lithium is around 3 mole percent impurity concentration, while that for boron occurs at a significantly higher concentration. It will be shown that at high enough impurity concentrations the solid becomes globally unstable and begins to undergo a complete phase separation into its two components. At lower concentrations, the solid is metastable and the intrinsic rate of pairwise impurity recombination can be estimated through the simulations. For the case of lithium, this intrinsic rate is much faster than the self-diffusion rate of the impurities, thus suggesting a diffusion-limited recombination process.

Solvation plays a crucial role in chemical reactions, including effects on reaction barriers and mechanisms. A notable example of this is found in the hydrolysis and condensation reactions leading to the formation of polyhedral oligomeric silsesquioxanes (POSS), a class of compounds with a multitude of DoD-relevant applications such as "next generation" plastics, high temperature insulators, and catalysts. Large reaction barriers are found for the hydrolysis and condensation reactions of isolated POSS precursors, but in the presence of one or more solvent molecules such as water, these barriers substantially decrease or even vanish altogether. The DoD centers have been instrumental in providing time for a detailed analysis of the water dimer potential energy surface. The results of these calculations, carried out at a very high level of theory, will provide the framework for a new, very accurate water potential. Even the best available water potentials do not include dispersion terms, and their electrostatic and repulsive contributions are not very accurate. In addition, most potentials do not include many body interactions. These limitations restrict the accuracy with which one can study the effects of solvation on chemical reactions. The new water potential that is being developed will therefore allow much more accurate simulations of solvation effects on chemical processes.

New materials with fast non-linear optical (NLO) response over broad spectral bandwidths and nano-structures for optical switching, which are critical for laser eye and sensor protection, are being explored. The design of such novel materials requires that material properties are carefully optimized, for example, to achieve large NLO coefficients, high conjugation, appropriate ground and

excited state absorption, as well as exhibit defined structural motifs, folding patterns and properties, especially when derivatized with NLO chromophores. In particular, we report the study of organometallic systems, such as phthalocyanines and porphyrins for optical limiting applications, as well as polymer dispersed liquid crystals (PDLC) and biomaterials for laser hardening applications.

1. High Energy Density Matter (HEDM)

1.1 Low Temperature HEDM

1.1.1 Background

Solid hydrogen doped with energetic impurities may form the basis for high energy density matter (HEDM) to be used in rocket propulsion. A key research priority is therefore the largescale computer simulation of impurity diffusion and recombination in HEDM in order to better understand the reasons for its stability, or instability, as the case may be. The recombination of these atomic impurities is an extremely exothermic reaction, and therefore thermodynamically favored. Theoretical developments within the Voth research group allow the quantum dynamical simulation of these systems, which is necessary to properly treat the problem. Classical molecular dynamics simulations, while less computationally challenging, predict qualitatively incorrect properties for low temperature liquid and solid hydrogen because of the highly quantum nature of the hydrogen matrix, and are therefore inadequate.

An immediate goal of the Voth group's AFOSR-supported Challenge project is to directly calculate from largescale computer simulation the relevant rates for the impurity recombination process. The primary effort since the initiation of the Challenge grant has been on largescale simulations of lithium and boron impurity diffusion and recombination in *para*-hydrogen at 4K, as well as in the development phase of an *ab initio* molecular dynamics code for HEDM synthesis studies also supported by AFOSR. Significant results are being obtained which are summarized in the next section.

1.1.2 Low Temperature HEDM Simulations: Results

The computer simulation of impurity trapping and mobility in quantum solids represents an extraordinary challenge because the solid is so strongly influenced by nuclear quantum effects. For example, the self-diffusion constant D is obtained from a *quantum dynamical time correlation function for velocity*. Low temperature HEDM systems thus require an explicit quantum dynamical treatment to calculate their relevant dynamical properties. Classical molecular dynamics (MD) approaches are completely inadequate.

A novel quantum dynamical approach which makes the study of HEDM systems possible has been developed in the Voth group which is called "Centroid Molecular Dynamics" (CMD). In the CMD approach, the impurity self-diffusion constant can be obtained through the correlation functions by running classical-like trajectories for the quantum particles on an effective, temperature-dependent potential. In the "exact" CMD algorithm, the effective potential is calculated "on the fly" by performing equilibrium quantum averaging simultaneously with the time-integration of the CMD equations. In fact, a "hyper-parallel" CMD algorithm (Calhoun, Pavese, and Voth, 1996) has been developed which has exhibited near linear performance scaling over 64 or more nodes in our simulations of liquid and solid hydrogen on various DOD computers (cf. Fig. 1). The theoretical breakthrough of CMD is thus allowing the Voth group to directly simulate the dynamics of quantum liquids and solids, as well as impurity diffusion and recombination in potential HEDM and related systems.

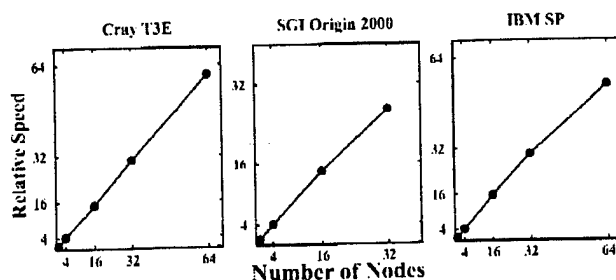


Figure 1: The scaling of the CMD algorithm on various platforms versus the number of nodes.

As a first step in this effort, the quantum barrier for the intrinsic recombination step between two lithium impurities has been determined (Jang and Voth, 1998.) The lithium atoms were initially placed in well-separated single substitutional sites in the *para*-hydrogen hcp lattice at 4 K and equilibrated. The barrier calculation first involved the computation of the equilibrium mean centroid force between the two lithium atoms for fixed distances, and then this force was integrated to determine the quantum free energy. The barrier occurs at a separation of 8.28 Angstroms and has a height of 80 K. It is interesting that the lithium nuclei actually tunnel due to their strong binding interaction. From the barrier height, the intrinsic recombination rate is estimated to be 1800 per second, which is significantly higher than the overall recombination rate observed in the experiments of Fajardo and co-workers at Edwards AFB. These results thus suggest that the impurity recombination may be diffusion-limited in the experiments, so this issue will be further explored in the future.

As a second step, the recombination of lithium impurities in "loaded" para-hydrogen solids was probed through the quantum dynamics simulations. Two systems were studied. The first was at 2.5 mole percent lithium impurity concentration, while the second was at 3.3 mole percent. Dramatically different behavior was observed between the two systems. Time-dependent Li-Li radial distribution functions were obtained from a long quantum trajectory for both systems. In the case of the 2.5 mole percent system, the lattice exhibited some relaxation, but the system was clearly stable on the timescale of the simulation (several nanoseconds). On the other hand, in the 3.3 mole percent system, a local recombination event between two lithium atoms occurred after the first ten picoseconds of the trajectory which, in turn, triggered a global instability of the system, leading to recombination and eventual clustering of all of the lithium impurities. This behavior can be seen in Figure 2 from the time-dependent behavior of the peak around 3 Angstroms in the Li-Li radial distribution function (i.e., the lithium dimer distance). These results suggest the lithium loaded para-hydrogen solid may be stable up to approximately 3 mole percent impurity concentration.

48 Lithium Atoms

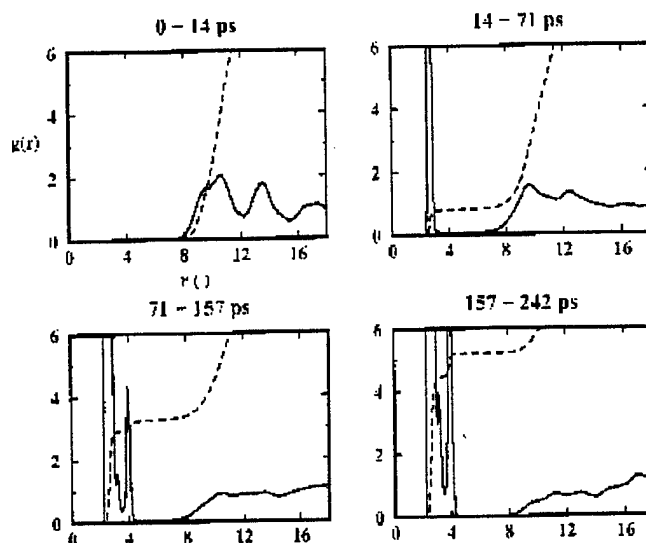


Figure 2: The time-dependent Li-Li radial distribution function for *para*-hydrogen loaded with lithium impurities at 3.3 mole percent.

In the most recent studies, the loading of boron in solid hydrogen has been explored. This potential HEDM is of a much greater priority for Air Force use. The preliminary results indicate the solid is stable up to 6 mole percent, even if two impurities are forcibly recombined. For example, it is seen in Figure 3 that no short range peak exists in the B-B radial distribution function (which would suggest dimer or cluster formation), even after a very long quantum MD run.

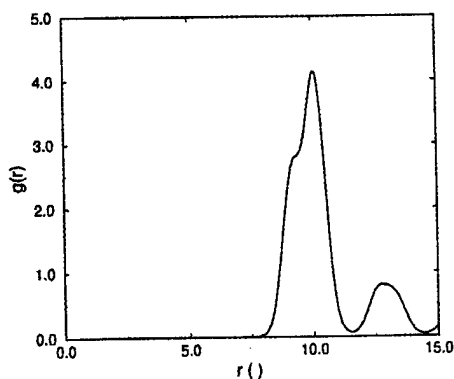


Figure 3: The B-B radial distribution function for *para*-hydrogen loaded with boron impurities at 6 mole percent.

1.2 HEDM Molecules

The theory component of the HEDM program has focused on the use of modern computational techniques to design new high energy species that have potential as new fuels. Dr. Robert Schmitt at SRI has proposed a series of 1,2,4-triazoles as potential HEDM candidates. This effort illustrates the importance of collaborations between theory and experiment, since none of these compounds has been synthesized, although likely routes have been mapped out. The role of theory here is to first determine the heats of formation for these compounds, then the specific impulse (Isp) to determine the raw HEDM potential. Based on these results, the next steps are to (a) examine the most likely unimolecular decomposition paths to assess the inherent stability, particularly the size of barrier heights,

(b) examine the reactivity with water (hydrolysis), oxygen, and other environmental species, (c) examine the potential energy surface for the lowest triplet excited state to determine the likelihood that the compound might predissociate via a repulsive triplet, and (d) develop a sufficiently accurate ground state potential energy surface to permit the study of solid state properties. The last two steps will be done in collaboration with Professors Yarkony (Johns Hopkins) and Thompson (Oklahoma State), respectively. To date, we have determined the heat of formation for the species shown in Figure 4 and shown that the corresponding I_{sp} is larger than that for hydrazine, a current fuel. The calculations on this compound are now being refined using second order perturbation theory, and calculations on the reactions of this species with water have been initiated. At the same time, the first series of calculations are proceeding on other triazoles. Both the IBM SP2 at Maui and the Cray T3E at CEWES have been indispensable for this project.

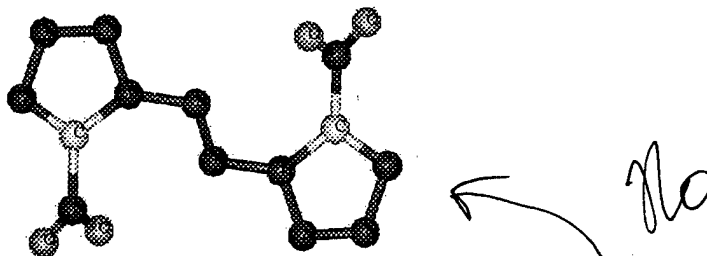


Figure 4. RHF/6-31G(d) optimized geometry of the high energy density molecule $C_2N_{10}O_4$.

A high energy density molecule which recently has been identified as a new candidate for a low sensitivity explosive is 1,1-diamino-2,2-dinitroethene (Bemm and Östmark, 1998). The presence of extensive intra- and intermolecular hydrogen bonds is thought to play a critical role in the low friction sensitivity of this compound. Calculations of the extensive intermolecular hydrogen bonding interactions involving up to seven monomers are currently underway. These calculations subsequently will be used to develop an accurate ground state potential energy surface to be used for predicting solid state properties (in collaboration with Professor Don Thompson, Oklahoma State University.)

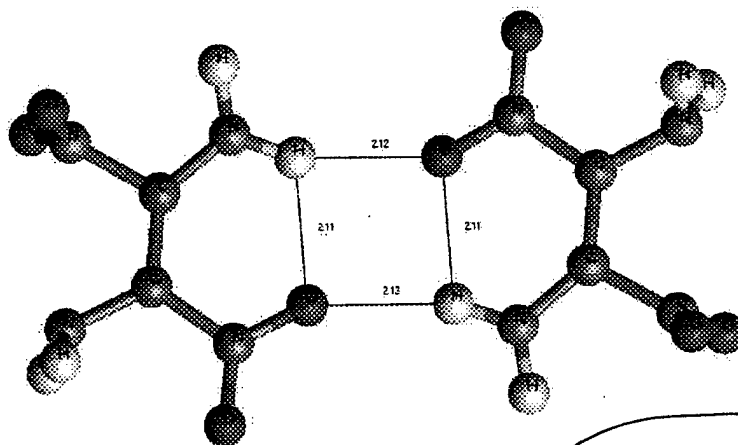


Figure 5. RHF/6-31G(d) optimized geometry of the "edge-to-edge" conformation of the 1,1-diamino-2,2-dinitroethene dimer.

Related to our studies of HEDM species is an analysis of the structure, heat of formation and decomposition pathways of the explosive molecules created when benzene rings are attached via polyacetylene linkages. Geometry optimization of the parent compound shown in Figure 6 are nearly completed at the Hartree-Fock level of theory. This will be followed by determination of the heat of formation using a combination of the G2 model and homodesmotic reactions.

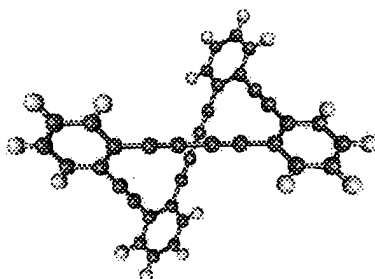


Figure 6. RHF/6-31G(d) optimized geometry of the $C_{36}H_{16}$ explosive annulene molecule.

2. Solvation Effects in Chemical Reactions

2.1 Mechanisms for Polyhedral Oligomeric Silsesquioxane Formation

Polyhedral oligomeric silsesquioxanes (POSS) show great promise as viscosity modifiers and materials precursors. There is therefore considerable interest among the synthetic community in exploring modifications of these species that might enhance their properties. However, virtually nothing is known about the mechanisms by which they form. Consequently, we have initiated a long term investigation of the POSS formation mechanism, with particular interest in overall thermodynamics, intrinsic barrier heights, and the effects of solvent, substituents and catalysts. In the first series of calculations, we investigated the most likely first two steps in the mechanism: hydrolysis of the starting material, trichlorosilane, to trihydroxysilane and the subsequent condensation of this product. The calculations were performed using second order perturbation theory for geometries and CCSD(T) with large basis sets for final energetics. The intrinsic barrier heights for all three hydrolysis steps and for the condensation reaction are all quite large, in the range of 20-30 kcal/mol, although the very step has by far the largest barrier. However, the effect of adding just one water molecule is dramatic. All predicted barriers except that for the first hydrolysis step fall to nearly zero, and that for the first hydrolysis step falls to about 7 kcal/mol. This is a striking result that demands investigation of the effects of additional water molecules as well as other solvents and catalysts. At the suggestion of our experimental colleagues, we have also initiated calculations in which (a) an acid molecule is added to the reaction mixture (b) substituent effects are being probed by substituting alkyl groups and methoxy groups for the silyl hydrogen and (c) using ammonia instead of water for the catalyst. Preliminary results suggest that the addition of one molecule of HCl does reduce the barrier, but by nearly as much as one molecule of water. Access to the IBM SP2 at MHPCC was essential for this work. The first manuscript on this work (Kudo and Gordon, 1998) has been published.

3. Non-linear Optical Materials

3.1 Optical Limiting Materials

In response to the need of providing a basic understanding of porphyrin-based optical limiting materials that exhibit the reverse saturable absorption (RSA) mechanism, systematic studies were carried out of the basic chromophores and their derivatives, with some results described below. Previously we investigated *meso*-alkynyl porphyrins (Wang, Day, and Pachter, 1998) and phthalocyanines in the gas-phase and in solution (Day, Wang, and Pachter, 1998). Most recently, a study on the effects of β -halogenation on the structure, electronic spectra, IP, and stability of free-base and zinc porphyrins (ZnP), which are important in predicting the performance of optical limiting materials, has been completed (Nguyen, Day, and Pachter, *J. Chem. Phys.*, in press). The results show large electronic effects upon halogenation; valence IPs of porphyrin increase significantly, with fluoro and chloro groups having essentially the same effect on the lowest IP of porphyrin. Similar effects are noted for ZnP. Since optical limiting materials have to be stable against direct photodegradations or other photo-induced reactions, our observation is an encouraging step towards the design of materials for laser hardening. In addition, a good RSA limiter has to demonstrate a sufficient long triplet lifetime and strong excited state absorption. The insight obtained from our electronic spectra calculations can be used as a reference point for studies of the triplet excited states to further tailor optical limiting properties. Indeed, electronic structure calculations of zinc octabrominated *meso*-tetraphenylporphyrins, which exhibit the largest experimentally determined optical limiting enhancement so far, were carried out to examine the ground state structures and spectra (Nguyen and Pachter, *JACS*, submitted), with some results described below. In addition, structure and energetics of the corresponding triplet excited states of these species were computed (Nguyen and Pachter, *JACS*, submitted). In contrast to the common assumption that the severe non-planar distortions observed from the X-ray crystal structures are principally responsible for the large red shift in the Soret and visible absorption bands, we found that geometry distortion contributes only partially to this observation. The results for substituted derivatives provide insightful accounts of the effects of phenyl, fluoro, chloro, and bromo substituents on the excitation energies. Work in progress includes calculations to predict the structures, energetics, and triplet-triplet spectra for the low-lying triplet states of free-base porphyrin. The singlet-triplet gap obtained is in excellent agreement with the experimental phosphorescence value, while excitation energies provide a good account of the observed T-T spectrum (Nguyen and Pachter, in preparation). A fundamental understanding of solvation is essential, and studies on the application of the Effective Fragment Potential (EFP) approach to assess solvent effects in optical limiting molecules that exhibit the two photon absorption mechanism are being carried out, in addition to the validation of the approach by a detailed study of water clusters (Day et al., in preparation).

3.2 Porphyrin Derivatives

Halogenation leads to significant changes in physical and chemical properties of porphyrins (Figure 7) that can be exploited in a wide variety of applications. We report results that examine the effects of *meso*-tetrahalogens upon the ground state spectra and the singlet-triplet (S_0-T_1) energy gaps. Calculations using density functional theory (DFT) were carried out to predict the structures and electronic spectra of *m*-PX₂H₂ (X = F, Cl, Br). The structures and energetics of the corresponding triplet states of these compounds were also computed to predict the triplet energy levels that can be directly compared with experimental phosphorescence values. The computed results may provide preliminary assessments of the spectroscopic properties prior to synthesis.

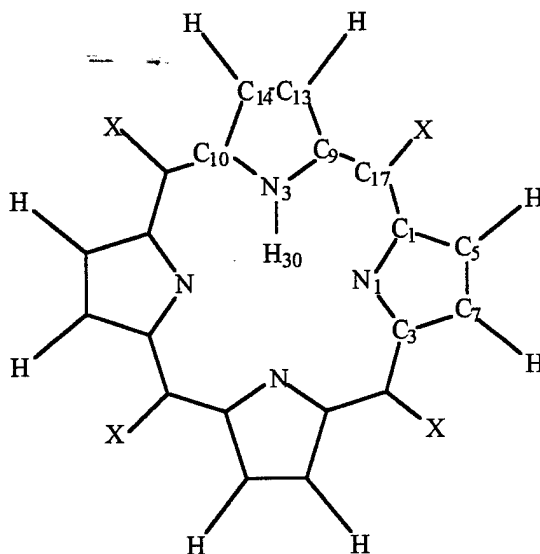


Figure 7: Porphyrin

Ground State Structures and Spectra. The ground state of all meso-PX₄H₂ species are predicted to have D_{2h} symmetry. In comparison with PH₂, changes in bond lengths of the porphyrin framework for all meso-PX₄H₂ are within 0.01 Å. All bond angles in meso-PX₄H₂ are within 2° of the corresponding angles in PH₂. The spectral shifts observed in meso-PX₄H₂, therefore, are largely of electronic origin. Our results reproduce the experimental excitation energies of PH₂ reasonably well up to the N bands. Upon fluorination, the Q band red-shifts about 0.1 eV. Chlorination and bromination also red-shift the Q bands (~0.2 eV). In comparison to β-octahalogenation, the shifts exerted by meso-tetrahalogenation to the Q bands are about twice as large in energy. In contrast to large red-shifts (~0.4 eV) previously observed for β-octahalogenation for the B bands, very small spectral shifts (0.04 eV to the blue for B_x, B_y is not shifted) are seen upon meso-tetrafluorination. However, the corresponding chlorination and bromination cause larger red-shifts (~0.2 eV) of the B bands. Similar spectral trends are also observed for the N bands. The meso-tetrafluorination of PH₂ causes slight shifts of 0.04 and 0.06 eV to the blue and red for the N_x and N_y band. Chlorination and bromination, however, red-shift the N bands by about 0.2-0.3 eV.

Triplet Excited State Structures and Energetics. For PH₂, the excited state structure was found to retain the D_{2h} symmetry. The macrocyclic ring was also allowed to undergo two different distortions, C_{2h} and C_{2v}. However, these structures converged to the D_{2h} equilibrium geometry after the optimization. Among the noticeable structural changes upon going from the ground to the first triplet excited state (T₁) are the stretching (0.03 Å) of one of the C_β-C_β (C₁₄-C₁₃) and C_β-C_μ (C₉-C₁₇) bonds and the shortening of one of the C_α-C_β (C₉-C₁₃) bonds by the same amount. Other bond changes involve a slight (0.01 Å) increase and decrease in the N₁-C₃ distance and C₁-C₁₇, respectively. For PH₂, changes in bond angles are no larger than 1° upon going from the ground to the first triplet excited state. Energetically, T₁ lies 1.53 eV above the ground state on the classical potential energy surface. Zero point corrections lower the S₀ → T₁ splitting of PH₂ to 1.42 eV. These predicted excitation energies are in good agreement with the experimental phosphorescence value of 1.58 eV. Small changes in geometry are observed upon meso-halogenation. The details are reported elsewhere (Nguyen and Pachter, *JACS*, submitted). The minimum structures for all meso-PX₄H₂ were also found to have the D_{2h} symmetry with stretched C_β-C_β and C_β-C_μ bond distances. The changes in the meso-PX₄H₂ skeletons upon going from S₀ to T₁ are essentially the same as the corresponding changes observed for PH₂. However, the electronic effects induced by meso-halogenation on the S₀ → T₁ splittings are large. In contrast to β-octahalogenation where S₀ → T₁ splitting is largely unaffected, meso-tetrahalogenation reduces the splitting by about 0.2 eV. There are small differences in S₀ → T₁ splittings among the meso-PX₄H₂.

3.3 Modeling of Liquid Crystals

In addition to our ongoing work to derive structure-to-property relationships for candidate liquid crystalline materials (Patnaik, Lupo, and Pachter, 1998), studies to model a polymer-dispersed liquid crystal (PDLC) system of interest were carried out (Patnaik and Pachter, in press). Recent work is in progress for studying a liquid crystalline droplet to model the behavior of a liquid crystal in the bulk, as described briefly below, with the details reported elsewhere (Wang et al., in press). Indeed, atomic level simulations are important in understanding the structure-property relations of materials. For example, the electro-optics of a PDLC can be tuned by varying its constituents. The understanding of the surface anchoring transition from homeotropic (normal) to homogeneous (in plane) of LCs on different polymer walls in the nematic temperature region will help the design of such materials. Due to the size of the LC droplet (typical in microns), very large-scale molecular dynamics (MD) simulations of such systems are required.

The most costly part of a large-scale MD simulation is the handling of long-range interactions, specifically the electrostatic non-bonded forces. An obvious direct calculation requires $O(N^2)$ operations per timestep to compute these forces. In many cases, the simple cutoff method is inappropriate. The method of Ewald summation improves the scaling to $O(N^{3/2})$, while the fast multipole method, which uses a multiscale hierarchy of partitions of the volume and a divide-and-conquer strategy to compute the power series, allows all the forces to be computed to any specified accuracy in $O(N)$ operations. In order to further improve the computing efficiency, we developed FMM3D (an implementation to FMM in 3-dimensional space), which contains a variety of schemes for computing multipole translations. This code has been incorporated into the MD (fast molecular dynamics) program we develop through the CHSSI program.

Calculations of a liquid crystalline system of 944 4-n-pentyl-4'-cyanobiphenyl (5CB) molecules were carried out using FMD. To our knowledge, this is the largest size simulation so far for a 5CB cluster with all atomic interactions considered. For the results reported in this section, the initial configuration of the simulation is a lattice of 944 5CB molecules or 35,872 atoms in a cube of size $81.8 \times 68.8 \times 68.8 \text{ \AA}^3$, consistent with the experimentally measured density at its nematic phase. The molecules are oriented along the longer dimension of the box with a nematic order parameter of ca. 0.6. The initial temperature is 300K, within the known range of its bulk nematic phase (295 to 308 K). Velocity was rescaled to stabilize the temperature. The MD time step is taken as 1 fs. The long-range interactions are updated in a cycle of 10 time steps. The number of multipole expansion terms is typically 6 and FMM finest cell level, L , is 4. The simulations were carried out to up to a time of 1.16 ns. The change of the system shape and molecular orientations on the surface are clearly demonstrated by analysis of the results, with the reconstruction and orientation order changes continuing throughout the simulations. The nematic order decreases significantly in the 25 to 35 Å radial region. Even near the center, the nematic order is continuously weakened up to 1 ns simulation time. This shows that the effect of the free surface on the orientation order is deep for this droplet size. Surface molecules tend to orient along the tangential of the sphere with some trends of bipolar order. To further investigate the effects of an external field and a structured wall of polymer matrix, larger simulations of such problems will be carried out. Indeed, this work is intended to be a first step for the full atomic scale study of liquid crystalline droplets in a polymer dispersed liquid crystal.

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